

Thermal behaviour and non-isothermal kinetics of $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ amorphous system

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Abstract : Differential thermal analysis DTA at different heating rates for $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ chalcogenide glasses are reported and discussed. Characteristic temperatures T_g , T_c and T_m were estimated at different heating rates. Cyclic scanning technique was used to investigate thermal induced phases during two consecutive heating-cooling cycles covering the temperature range $T_g - T_m$.

The effective activation energy (E), the order (n) and the rate (k) of crystallization along with the growth (m) under non-isothermal conditions are also reported. Obtained results were treated according to Johnson-Mehl-Avrami and modified Kissinger approaches.

Keywords : Chalcogenide glasses, thermal analysis.

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1. Introduction

Semiconducting chalcogenide glasses of Ge-Se-Te system have received attention because of their important optical application in the infrared region. The glass-forming region in the Ge-Se-Te system exists in two sections :

- (i) Compositions with excess Se,
- (ii) Compositions with large Ge and Te content. The GeSe_2 -Te was found to form the boundary between these two regions. The connectedness varies from two (Se and Te) to four (Ge) in such glass systems, where the bonding is essentially covalent. The investigated systems were subjected to different studies [1–3].

Studies of kinetics are always connected with the concept of activation energy. The value of this energy in glasses is associated with nucleation and growth mechanisms that dominate the devitrifications of most glassy solids. Studies of the crystallization of a glass upon heating can be performed in several different ways, isothermal and non-isothermal.

The aim of the present work is concerned with the study of the crystallization kinetics of $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ ($x = 16.65, 13.35$ and zero) system. Different methods have been discussed to evaluate the associated activation energies applying the non-isothermal technique. Moreover, DTA data were correlated with characteristics differences between a structurally stable materials (exhibiting switching phenomena) and a reversible materials (exhibiting memory phenomena).

2. Experimental method

High purity (99.999%) Se, Ge and Te in appropriate proportions were weighted in silica tubes. The tubes were sealed under a vacuum of 1.3×10^{-2} Pa and heated in a furnace at 200°C for two hours. The furnace temperature was raised up to 1000°C with rate of 200°C per hour. The synthesis was continued for six hours during which the molten materials were occasionally shaken vigorously to ensure the homogeneity of the samples. The melts were then rapidly quenched in ice-water with the tube in a horizontal position.

The obtained quenched materials of the $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ system were identified as glasses due to their bright fractures except $x = 0$. The ingots were confirmed to be completely amorphous or partially by X-ray diffraction and differential thermal analysis (DTA), as shown in Figures 1 and 2.

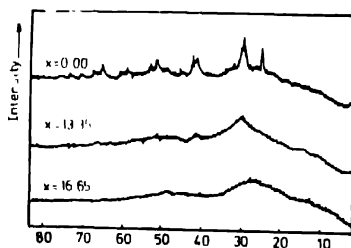


Figure 1. X ray diffraction patterns for (a) Bulk $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ with different compositions $x = 16.65, 13.35$ and zero

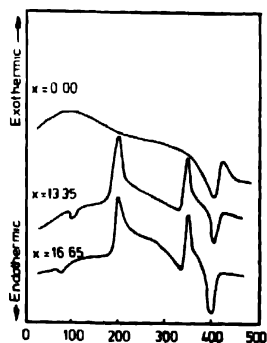


Figure 2. Differential thermal analysis DTA thermograms for glassy $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ systems ($x = 16.65, 13.35$ and zero) at $10^\circ\text{C}/\text{min}$

DTA thermograms were obtained using the powder of freshly quenched (as prepared) material, 25 mg was put in an aluminum sample pan. The latter was immediately introduced in its place in the DTA apparatus (Shimadzu model DT-30) and a constant heating rate was applied. The differences ΔT , between the sample temperature and that of

the reference ($\alpha\text{-Al}_2\text{O}_3$) were recorded directly as a function of the furnace temperature (T) using a double-pen recorder. Heating rates of $\phi = 2, 5, 10, 20, 30$ and $50^\circ\text{C}/\text{min}$ were used as shown in Figure 3.

3. Results and discussion

3.1. Effect of composition and heating rate on thermal transition :

DTA traces at rate of $10^\circ\text{C}/\text{min}$ of freshly prepared $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ where $x = 16.65, 13.35$ and zero, are shown in Figure 2. The traces follow the known common behaviour, where the three characteristic temperatures T_g , T_c and T_m are observed and given in Table 1.

Table 1. Data data of the investigated glasses in $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ system, the temperatures are given in ($^\circ\text{C}$).

Comp	Rate	T_g	1st peak			2nd peak			T_M	
			T_c start	T_c max	T_c end	T_c start	T_c max	T_c end	T_M start	T_M end
$x = 16.65$	5	60	182	196	206	330	340	345	—	400
	10	70	185	198	210	334	345	350	—	395
	20	70	190	200	212	—	350	—	—	390
	30	90	190	202	220	—	365	—	—	395
	50	150	215	225	242	—	395	—	—	402
$x = 13.35$	2	—	185	192	202	325	335	345	—	—
	5	—	175	195	200	330	340	345	—	405
	10	90	185	200	210	335	335	357	380	400
	20	105	200	205	232	—	370	—	—	405
	30	125	—	235	—	—	372	—	—	397
	50	150	235	240	275	—	390	—	—	405

Compositions of $x > 0$ exhibit two crystallization peaks and one melting peak. On the other hand, for $x = \text{zero}$ there is a broad crystallization peak followed by a melting peak. This is most likely due to the partial crystallinity of the latter composition, as shown in Figure 1.

The effect of heating rate on the characteristic temperatures was investigated at six different rates for $x = 16.65$ (as an example and shown in Figure 3 the data listed in Table 1). The observed T_g of a glass is increased by increasing the heating rate, inspection of obtained data. For an ideal glass there, is a lower limit to this change. But for this system, the wide range of changes in T_g indicates that this system behaves as a normal glass.

It is worthy to mention that for $x = 16.65$ and 13.35 , the DTA scan at $\phi = 2^\circ\text{C}/\text{min}$ shows that a small amount of the sample material has been crystallized. The crystallization of amorphous material proceeds by the processes of nucleation and growth. Moreover, the crystallization rate is suppressed by reducing the rate of nucleation or the rate of growth. Since growth follows nucleation, in some cases if the nucleation is prevented, there will be no crystallization. However, even if nucleation occurs, the crystallization rate can still be suppressed by reducing the rate of growth. Turnbull [4] indicates that the growth rate in

liquids with high viscosity is limited. So, perhaps at the heating rate of $2^{\circ}\text{C}/\text{min}$, the liquid will reach the maximum rate of crystallization when the viscosity is still high.

3.2 DTA cyclic scanning :

Thermal cycling has been performed up to 450°C . For composition $x = 13.35$ (as an example), the degree 450°C was chosen such that the maximum temperature is far from the decomposition temperature

The DTA cycling has been performed as follows :

Run (a) : the DTA temperature was raised from room temperature up to 450°C at heating rate $15^{\circ}\text{C}/\text{min}$.

Run (b) : lower the temperature down to 50°C at the natural cooling rate of the DTA device, i.e. at an average rate of about $15^{\circ}\text{C}/\text{min}$, followed by another cycle heating run (c) and cooling run (d).

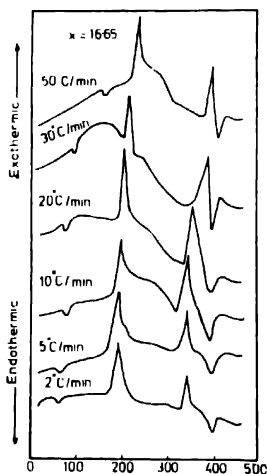


Figure 3. DTA thermograms for $x = 16.65$ at different heating rates.

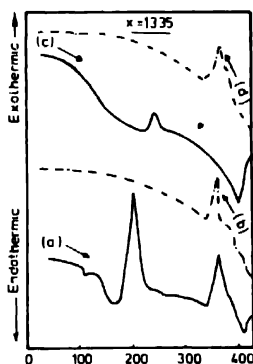


Figure 4. DTA scanning compositions for $x = 13.35$. Full and dashed lines are the respective heating and cooling curves at $15^{\circ}\text{C}/\text{min}$.

For composition $x = 13.35$ as an example, and shown in Figure 4, the value of T_g detected on first heating run (a) for $x = 16.65$ at 70°C and for $x = 13.35$ at 105°C . Also, one melting peak in the range 390°C for $x = 16.65$ and 410°C for $x = 13.35$ and two crystallization peaks were observed for both compositions $x = 16.65$ and 13.35 in the range $200\text{--}360^{\circ}\text{C}$. This is most likely due to segregation of two phases. In run (b), during the first cooling, one solidification peak has been detected in the range $355\text{--}370^{\circ}\text{C}$, in case of $x = 16.65$ and 13.35 . In heating run (c) (the second heating cycle), the T_g disappeared and a broad T_c peak moved to a higher temperature for $x = 13.35$, 16.65 and listed in Table 2. This is probably connected with the morphology of the sample; before run (a), the material

was in the powder form, but before run (c) it was in the solid form. It was observed that the growth of crystals was more readily from powdered glass than from large solid pieces. It can be concluded that the glass forming tendency is weak for the high Te content. Moreover, for compositions $x > 0$, the phase separation appears. This is related to the Ge-Te and Ge-Se according to the chemical bonds.

Table 2. Transition temperatures during two consecutive heating-cooling DTA cycles ($^{\circ}\text{C}$) of the ternary glassy $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ systems

	$x = 16.65$				$x = 13.35$			
	T_g	T_{c1}	T_{c2}	T_m	T_g	T_{c1}	T_{c2}	T_m
Run (a)	70	205	355	395	105	200	360	405
Run (b)	–	–	370	415	–	–	360	–
Run (c)	–	200	–	400	–	240	–	400
Run (d)	–	–	370	415	–	–	365	–

The above arguments allow to conclude that the investigated compositions belong to reversible class of materials. In other words, their structures can be changed reversibly between two structural states located at the border of the glass forming regions.

It is well mentioned that chalcogenide glasses exhibit many useful electrical properties including threshold and memory switching. The electrical properties are influenced by the structural changes associated with thermal effects and can be related to thermally induced transitions [5]. The glasses which exhibit no exothermic peaks in the cooling runs, display very little tendency to crystallization. This is usually belongs to threshold switching type. But the glasses which exhibit an exothermic crystallization peak in cooling runs, display high tendency too crystalline, and they are memory-switching type. The latter case is clearly observed for the glassy composition rich in Te, which causes thermally induced microphase separation and subsequent crystallization of Te [6].

3.3. Crystallization kinetics :

Studies of kinetics are always related to the concept of activation energy. The values of this activation energy in glass crystallization phenomena are associated with nucleation and growth processes that dominate the devitrification of most glassy solids [6,7–9]. Two basic methods can be used for knowing the crystallization of a glass upon heating, isothermal and non-isothermal. In the former, the sample is brought quickly to a temperature above the glass transition temperature T_g and the heat evolved during the crystallization process at a constant temperature is recorded as a function of time t . In the non-isothermal method, the sample is heated at a fixed rate α , and the heat evolved is recorded as a function of temperature or time. The isothermal crystallization data is usually interpreted in terms of the Johnson-Mehl-Avrami (JMA) transformation equation [9–12].

The evaluation of non-isothermal activation energy for crystal growth has been estimated by a large number of mathematical treatments based on the formal theories of transformation kinetics. The theories differ greatly in their assumptions and in some cases, they lead to contradictory results. Partial area analysis and peak shift analysis are the basic method for all mathematical treatments.

3.3. (a) Peak shift analysis :

The peak shift technique is based mainly on the systematic variation in the peak temperature of crystallization with the heating rate.

- (i) The activation energy (E) for any crystallization mechanism can be calculated from two different thermograms by the following equation [13] :

$$E = R \frac{T_p T_p'}{T_p - T_p'} \ln (\phi / \phi') (T_p' / T_p)^2, \quad (1)$$

where ϕ and ϕ' are two different heating rates, and T_p and T_p' are the corresponding temperatures of the crystallization peaks. Combinations between different heating rates were made to compute the average E values, which are listed, in Table 3.

- (ii) The Kissinger formula was used for homogenous crystallization [14] or in other words, surface nucleation dominates and $n = 1$.

$$\ln (\phi / T_p^2) = -E / RT_p + \text{constant}. \quad (2)$$

The plots of $\ln (\phi / T_p^2)$ vs $1/T_p$, which are shown in Figure 5, are well fitted by straight lines. From the slopes of these lines, the activation energy of crystallization E can be estimated and are listed in Table 3.

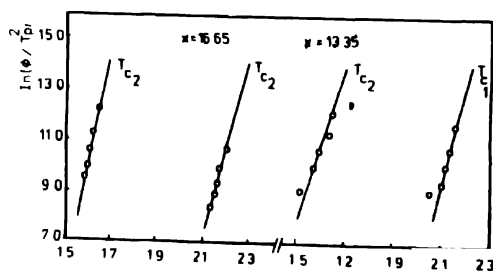


Figure 5. The relation between $\ln (\phi / T_p^2)$ and $10^3 / T_p$ for $x = 16.65$ and 13.35 .

- (iii) The approximation due to Mahadevan *et al* [6] was used, where the variation in $\ln (1/T_p^2)$ with $\ln \phi$ is much less than that $1/T_p$ with $\ln \phi$. Therefore, eq. (2) can be written in the form

$$\ln \phi = -\frac{Ec}{RT_p} + \text{constant}. \quad (3)$$

Table 3. The thermal parameters of the ternary glassy $\text{Ge}_{10-x}\text{Se}_{40}\text{Te}_{50-x}$ systems for the two crystallization peaks. E values are given in eV/atom

Peak order of cryst	Comp	Avrami method		Math. average \bar{E}	Kissinger method		Mahadevan approx		Modified Kissinger method	
		n	E		$\ln k$	E , when $n = m = 1$	E , when $n = m = 1$	E , when $n = m = 1$	E	m
First peak	$x = 16.65$	2.10	2.40	-5.2	2.34	2.88	2.88	2.43	4	3
	$x = 13.35$	2.85	3.67	-8.0	2.65	3.29	3.44	3.44	1	1
Second peak	$x = 16.65$	1.75	3.67	-3.80	3.21	3.71	3.71	3.10	3	2
	$x = 13.35$	3.47	5.71	-7.90	3.28	2.89	2.71	5.10	2	1

A plot of $\ln \phi$ vs $1/T_p$ for $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ gives a straight line, as shown in Figure 6. The value of E obtained from the above method is listed in Table 3.

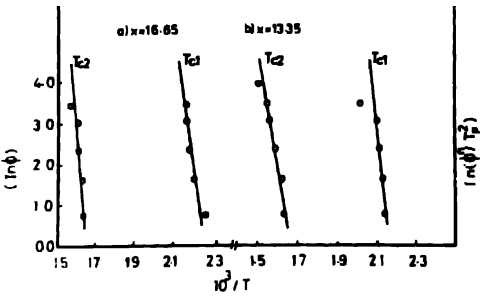


Figure 6. The relation between $\ln \phi$ and $10^3/T$ for $x = 16.65$ and 13.35

(iv) The modified Kissinger-method :

In this method, the relation between the rate ϕ and the crystallization temperature T_p is assumed to have the following form :

$$\ln \left(\phi^n / T_p^2 \right) = - \frac{mE}{RT} + \text{constant} \quad (4)$$

If the crystallization mechanism is precisely known and it does not change with the heating rate, the plot of $\ln (\phi^n / T_p^2)$ vs $1/T_p$ gives the value of mE . Dividing mE by m , the activation energy for crystal growth can be obtained as shown in Figure 7. In eq. (4), m and n are integers having values between one and four. When nuclei are formed on heating at constant rate, n is equal to $(m+1)$ [6].

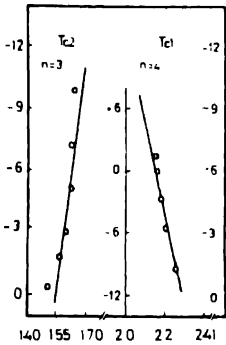


Figure 7. The relation between $\ln \phi^n / T_p^2$ and $10^3/T$ for modified Kissinger, for $x = 16.65$ and 13.35

All techniques depending on peak shift, lead to different relationships between the temperature of maximum crystallization rate T_p , and the heating rate ϕ . Such methods have the disadvantage that they neglect both the nucleation and the crystal growth rate K , the latter being active at the involved temperature range. The modified Kissinger method

facilitates the estimation of activation energy and rate of growth. However, the order of crystallization is usually obtained by other technique.

3.3. (b) Partial area technique :

In this technique, the relation between sample temperature T and heating rate ϕ can be written in the form

$$T = T_0 + \phi t, \quad (5)$$

where T_0 is the initial temperature. The estimation of the complex activation energy of crystallization (E) was obtained using Piloyan *et al*'s method [15] which is based on the differential form of the model relation for (α) known as $g(\alpha)$ and on Borchard's assumption [16]. According to them the reaction rate $d\alpha/dt$ is proportional to the temperature deflection ΔT , as detected by DTA. This means that the kinetic (JMA) equation [17] :

$$-\ln(1-\alpha) = k_0 t^n \exp(-E/RT) \quad (6)$$

can be applied to non-isothermal conditions after some modifications [6,9,18–20]. To apply JMA equation for non-isothermal technique, the region of cursory check [21] should be considered, namely the fraction α transformed at T_p should be ≈ 0.60 – 0.63 . For $\text{Ge}_{10+x}\text{Sc}_{40}\text{Te}_{50-x}$ glasses with $x > 0$, values of α at T_p satisfy this condition. Differentiation of JMA equation yields :

$$d\alpha/dt = nk_0^{1/n} \exp[-E/RT]^{1/n} F(\alpha), \quad (7)$$

$$\text{where } F(\alpha) = (1-\alpha)[-Ln(1-\alpha)]^{n-1/n} \quad (8)$$

Here, k_0 is considered to be constant with respect to temperature. For a constant heating rate $\phi = dT/dt$, eq. (7) is separable in α and T and can therefore, be directly integrated

$$\int_0^\alpha \left\{ d\alpha / (1-\alpha) \left[\ln(1-\alpha)^{-1} \right]^{n-1/n} \right\} = \frac{nk_0^{1/n}}{\phi} \int_0^T \exp\left(\frac{-E}{nRT}\right) dT. \quad (9)$$

This yields to

$$\left[\ln(1-\alpha)^{-1} \right]^{1/n} = \frac{Ek_0^{1/n}}{\phi R} p(x) = g(\alpha), \quad (10)$$

where $x = E/nRT$, the behaviour of the exponential integral functions $P(x)$ for different types of approximations has been reviewed in [22]. For a limited range, *i.e.* normal temperature interval of about 100°C , $P(x) = \exp(x)$. Therefore, eq. (9) can be written in the logarithmic form as

$$\log[g(\alpha)] = C - \frac{E}{2.303nRT}, \quad (11)$$

where C is constant.

Calculation of the function $g(\alpha)$ has been carried out by Stava and Skavara [23] for different reaction kinetic equations. A plot of $\log [g(\alpha)]$ against $1/T$ should yield a straight line over the whole range of α ($0 < \alpha < 1$) when the appropriate mathematical description of the reaction is employed. The slope of such straight line, is used to evaluate E/n . Typical plots of $\log [g(\alpha)]$ against $1/T$ are given in Figure 8, for the two crystallizations peaks. According to Sharp *et al* [24], it was observed that the function $A_3(\alpha)$, where $[-\ln(1-\alpha)]^{1/3} = Kt$, fits the obtained experimental results over a maximum range of α is almost 0.01 to 0.99 with the except of the second crystallization peak of the composition $x = 13.35$, where α is in the range of 0.01 to 0.68.

According to Avrami's equation (15)

$$\alpha = 1 - \exp(-Kt^n), \quad (12)$$

which can be written in logarithmic forms as

$$\ln[-\ln(1-\alpha)] = \ln k + n \ln t. \quad (13)$$

A plot of $\ln[-\ln(1-\alpha)]$ against $\ln t$, as shown in Figure 9, should yield a straight line whose slope is the order of crystallization (n) and intercept on the ordinate at $\ln k$. The value of n , which reflects the nucleation rate and the growth morphology is correlated with the effective activation energy (E/n), obtained from eq. (11). The values of n , k and E are evaluated and are given in Table 3. The plots are linear over most of the temperature range.

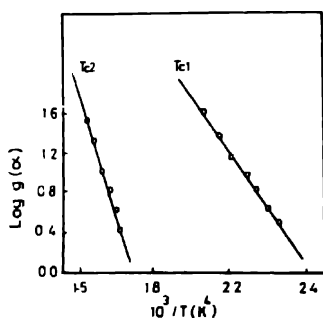


Figure 8. Plots of $\log [g(\alpha)]$ versus $10^3/T$ for the reaction kinetics $A_3(\alpha)$ for $x = 16.65$

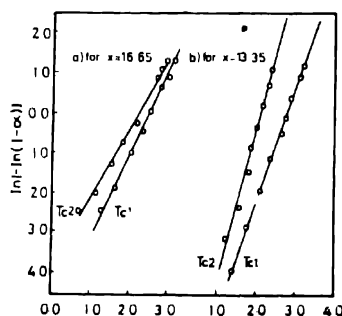


Figure 9. The relation between $\ln [-\ln(1-\alpha)]$ vs $\ln t$ for $x = 16.65$, $x = 13.35$.

At high temperature, or in regions of large crystallized fractions, a break in the linearity, or rather a lowering of the initial slope, is seen. Breaks of similar nature have been reported for many chalcogenide glasses, a naturally occurring oxide glass and two metallic glasses [25–27]. Generally, this break in slope is attributed to the saturation of nucleation sites in the final stages of crystallization [27,28] or to the restriction of crystal growth by the small size of the particles [29]. In all these cases, the analysis is confined to the initial linear region, which extends over a large range [25,26].

The partial area allows direct estimation of more parameters such as order of crystallization and rate of activation energy by single slow scan, which realized the non-isothermal condition.

Conclusion

The systematic study of the thermoanalysis of different compositions $\text{Ge}_{10+x}\text{Se}_{40}\text{Te}_{50-x}$ where $x = 16.65, 13.35$ and zero, using DTA technique indicates that :

1. The glass transition temperature T_g rises by increasing the heating rate as a result of increase heat capacity and the excess of the degrees of freedom that the material posses supercold liquid state.
2. By increasing the heating rate, the crystallization temperature increases due to the reduction in crystal growth.
3. The two compositions $x = 16.65$ and 13.35 are characterized by two crystallization peaks revealing the formation of two phases during the heat treatment.
4. Sample of $x = 0$ exhibits broad crystallization peak indicating partial crystallinity. This was confined by X-ray diffraction.
5. It is also observed that the melting peaks are independent of the heating rate which is a common behaviour.
6. According to the behaviour of $x = 16.65$ and 13.35 during the two cycles, we can conclude that these compositions having the ability for memory switching.
7. Many techniques, such as single-scan and multiscan techniques, were applied to evaluate the activation energy (E), the order (n) of crystallization, the rate of crystallization (k) and the order of crystal growth (m). The activation energy of crystallization is increased by increasing the ratio of Te for the two phases.
8. The excess of Te increases the freedom in bonding. This is confirmed by the order of crystallization (n) which is low for $x = 16.65$ (two-dimensional crystal growth) and increased for $x = 13.35$ (three-dimensional).

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